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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

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By C. Loring Jackson and Waldemar Koch.

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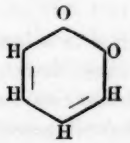
Attempts to prepare the orthobenzoquinone



have been mentioned, so far as we can find, in only two papers. The first is that by Zincke,† in which he describes tetrabromorthoquinone and tetrachlororthoquinone, but says that a number of attempts to make the unsubstituted orthoquinone have failed to produce the desired result. The second is by Hinsberg and Himmelschein,‡ who obtained orthodioxydiphenylsulphone by the action of potassic dichromate on a mixture of pyrocatechine and benzolsulphinic acid, and draw the inference that the formation of this substance probably was preceded by the formation of orthoquinone. They add that all their experiments to isolate orthoquinone have failed because of its strong tendency to condensation and polymerization.

It seemed to us that one probable cause of the ill success of these experiments was the sensitiveness of the orthoquinone to oxidizing agents; this view was confirmed by the observations of Cousin,§ that trichlorpyrocatechine and dibrompyrocatechine give only red resinous products with

* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Philosophy by Waldemar Koch.

† Ber. d. chem. Ges., XX. 1776 (1887).

‡ Ber. d. chem. Ges., XXIX. 2025 (1896).

§ Annales de Chim. et de Phys., [7] XIII. 485.

nitric acid, whereas the trichlor- or tribrom-homopyrocatechine gives under the same conditions an orthoquinone; and also by some experiments undertaken by H. A. Torrey and one of us on the action of hydric dioxide or electrolytic oxygen on pyrocatechine, which led to unpromising black products. Accordingly we searched for a method which would produce a quinone without the use of an oxidizing agent, and found one in the action of iodine on the lead salt of the dioxybenzol. After having shown that the method converted hydroquinone into quinone, we applied it to pyrocatechine; but our first experiments led to no result, because we used alcohol as our solvent, which attacks the orthoquinone as soon as it is formed. Upon replacing the alcohol by chloroform we succeeded in obtaining a dark garnet red solution, in which the presence of orthobenzoquinone was established by a number of tests given later in this paper.

From this solution we next tried to isolate the solid orthoquinone, but after trying every method we could devise, which gave even a remote promise of success, we have failed to obtain a trace of solid orthoquinone, and are forced to the opinion that it cannot exist in the solid state, or even for any length of time in solution. The products obtained in place of the orthoquinone in every case were a black substance insoluble in chloroform, and a brown substance, or mixture of substances, which dissolved in chloroform; this brown product we have not attempted to investigate, but we have studied the black insoluble product, and can give a fairly complete account of its nature in spite of its unmanageable properties. It begins to form in the chloroform solution of the orthoquinone in less than an hour, and is best obtained by allowing the solution to stand in a corked flask for not more than thirty hours. A combustion of the substance gave results corresponding to the formula $C_{12}H_8O_5$; the analysis of a lead salt prepared in a somewhat different way indicated the same formula, and this was confirmed by two analyses made by H. A. Torrey of his product from the electrolytic oxidation of pyrocatechine, which seemed to be identical with ours, and by an analysis of the benzoyl derivative of our black substance; we have, therefore, five analyses of four different samples, all of which agree with each other, and leave no doubt that the substance is a definite compound, and has the formula $C_{12}H_8O_5$. This formula indicates that the compound was formed by the union of two molecules of orthoquinone with the introduction of an additional hydroxyl group, a view which is confirmed by the analysis of the lead salt $C_{12}H_6O_5Pb$, in which there are evidently two benzol rings to each atom of lead. When we consider the manner in which these two benzol rings

are united, two theories seem especially worthy of attention: first, the two rings may be joined directly, so that the compound is a substituted diphenyl, (I.) $O_2(HO)H_2C_6\text{-}C_6H_3(OH)_2$; or second, they may be united by two atoms of oxygen forming a substituted pyrocatechine ether according to this formula: (II.) $(HO)H_3C_6\text{=}O_2\text{=}C_6H_2(OH)_2$* The first (diphenyl) formula is rendered much more probable than the second by the analogy between our orthoquinone and the orthonaphthoquinone, which is converted by dilute sulphuric acid into dinaphthyldiquinhydrone,† $O_2H_5C_{10}\text{-}C_{10}H_5(OH)_2$, a black powder like our alteration product; this has been proved by Korn ‡ to be a dinaphthyl body by conversion into α-α dinaphthyl and diphthalylic acid, $(COCO)(C_6H_4COOH)_2$. The support of the diphenyl formula by this analogy is so strong that we should feel it was hardly worth while to consider the second (ether) formula, if it were not for the fact that we have observed an oxygen attachment similar to that in Formula II. in a derivative of tetrabromorthoquinone, described later in this paper. To decide between Formula I. and Formula II. we studied the action of reducing agents on the black substance, as, if it were an ether (Formula II.), it should be reduced to a mixture of pyrocatechine and a trioxybenzol; whereas a diphenyl compound (Formula I.) would only take up two atoms of hydrogen without decomposition.§ We selected as the reducing agent sodium amalgam and water, because this had proved effective in breaking up the pyrocatechine ether containing bromine already alluded to; but, even after long continued action on our black alteration product, not a trace of pyrocatechine could be detected; the only reduction product was a black substance evidently as complex as the original body. This result, therefore, declares decisively in favor of the diphenyl structure (Formula I.).

The action of benzoylchloride on the black substance in presence of sodic hydrate converted it into a tribenzoyl derivative, $C_{12}H_5O_2O_3(COC_6H_5)_3$, thus proving the existence of three hydroxyl groups in the substance; and this benzoyl derivative, and also the original black compound, gave new substances with phenylhydrazine, which contained nitrogen, as was shown by the analyses. Unfortunately the percentage of nitrogen found in both cases was far below that required by the probable formulas, which

* In both these formulas the third hydroxyl group may be attached to the other benzol ring.

† Stenhouse and Groves, Ann. Chem. (Liebig), CXCIV. 205.

‡ Ber. d. chem. Ges., XVII. 3020.

§ Korn did not succeed in splitting dinaphthyldiquinhydrone into simpler bodies by reduction. — Ber. d. chem. Ges., XVII. 3024.

is undoubtedly accounted for by the difficulty in purifying these amorphous and infusible substances; our analyses, therefore, amount only to qualitative proofs of the presence of nitrogen. The introduction of the nitrogen, however, makes it highly probable that both the original substance and its tribenzoyl derivative contain oxygen atoms in the quinone position. We feel justified from the results of the foregoing experiments in assigning to the black alteration product the formula $O_2(HO)H_2C_6\text{-}C_6H_3(OH)_2$, in which two of the hydroxyl groups are probably in the ortho position to each other, since the substance forms a stable lead salt when treated with plumbic acetate.

We have made no progress toward determining the position of the third hydroxyl group, which may even be attached to the other benzol ring. The introduction of this third hydroxyl group is not without analogy, since the dinaphthylorthoquinone $C_{10}H_5O_2\text{-}C_{10}H_5O_2$ is converted by the action of the air on its solution in weak alkali into the dioxy compound $C_{10}H_4OHO_2\text{-}C_{10}H_4OHO_2$.* In our case, however, the oxygen of the air took no essential part in the reaction, as the same alteration product was formed in an atmosphere of carbonic dioxide; and this is not surprising, as we have had frequent occasion to observe that the orthobenzoquinone is a much stronger oxidizing agent than the orthonaphthoquinone, so that one portion of it might easily oxidize the other during the polymerization. The portions of the orthoquinone which gave up oxygen during the formation of the black body were undoubtedly converted into the brown substances soluble in chloroform, which made up about half of the total product.

Although, as has been already stated, we could not obtain the orthoquinone in the solid state, many of its properties can be determined from the study of its solution in chloroform; thus, there can be little doubt that it has an intense red color and little if any odor, as the solution smelt of nothing but chloroform, whereas a smell as strong as that of paraquinone could have been detected even in presence of the amount of chloroform used. Its very slight stability has been dwelt on at sufficient length already, but we should add that it seems to be decomposed at once by even small quantities of water or alcohol.

We turn next to the reactions of the solution on which is based our inference that it contained orthoquinone. Hydrochloric acid converted it into monochlorpyrocatechine, which, however, was mixed with a little pyrocatechine, as would be expected, since Wichelhaus† has shown that

* Korn, Ber. d. chem. Ges., XVII. 3021.

† Ber. d. chem. Ges., XII. 1504.

the action of hydrochloric acid on parabenzoquinone consists in the formation of hydroquinone and chlorine, which subsequently react together, and in this corresponding case part of the pyrocatechine formed could well have escaped the substituting action of the chlorine. Reducing agents like ammonic sulphide or sulphurous dioxide produced pyrocatechine from this chloroform solution. Bromine formed with it tetrabrompyrocatechine, the reduction of the orthoquinone being achieved in this case by the hydrobromic acid formed in making the substituted quinone.

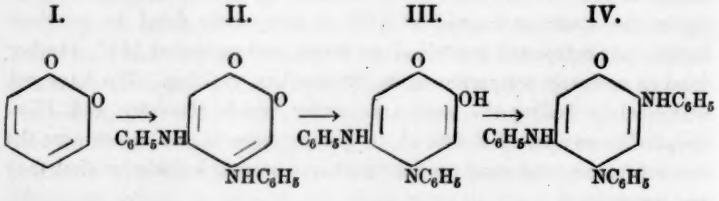
When the chloroform solution was added drop by drop to a solution of benzolsulphinic acid also in chloroform, an orthodioxydiphenylsulphone, $C_6H_5SO_2C_6H_3(OH)_2$, melting at 153° was formed, which should be identical with that obtained by Hinsberg and Himmelschein * by oxidizing pyrocatechine in presence of benzolsulphinic acid, but the properties of the two substances show they are different. Hinsberg and Himmelschein's substance contained water of crystallization, and melted at 117°, if this were not driven off; at 143° to 145° after heating in the steam-bath; and at 164° if completely dried by previous fusion; our compound contained no water, and melted at 153°, whether dried at ordinary temperatures or by previous melting. We have not succeeded in finding the conditions under which Hinsberg and Himmelschein's compound is formed, so that we were unable to compare the two substances, and must consider with our present knowledge that they are isomeric.

With aniline the chloroform solution gave a dianilidoquinoneanil, $C_6H_2(C_6H_5NH)_2O(C_6H_5N)$, which melted at 203°, and by this and a careful comparison of its other physical properties was proved to be identical with the body prepared by Zincke and von Hagen † from paraquinone by the action of aniline and acetic acid. As this substance has previously been made only from paraquinone, it has always been supposed that it contains the oxygen and anil group in the para position to each other, but after our preparation of it from orthoquinone it is also possible that it is a derivative of orthoquinone; and some weight is given to this view by the fact that it is formed easily from the orthoquinone by aniline alone, whereas it can be prepared from the paraquinone only with difficulty, and by the combined action of aniline and acetic acid. On the other hand, it seems hardly prob-

* Ber. d. chem. Ges., XXIX. 2025.

† Ber. d. chem. Ges., XVIII. 785

able that a derivative of orthoquinone would be so stable as this; and the beta-naphthoquinone forms with aniline and alcohol a corresponding anilidonaphthoquinoneanil, $C_{10}H_5O(C_6H_5NH)(C_6H_5N)$, which is undoubtedly a derivative of alpha-naphthoquinone. Zincke* also has obtained recently from the azimidodichlororthoquinone by warming it with aniline an azimidoanilidomonochloroxyparaquinone, and similar cases of conversion of orthoquinones into derivatives of paraquinones are not rare. We are so strongly of the opinion, therefore, that our dianilidoquinoneanil is a para body with the constitution O, 1. C_6H_5N, 4. $(C_6H_5NH)_2$, 2. 5, that we have not thought it worth while to submit the question to an experimental investigation, which would of necessity occupy much time. Assuming that the constitution given above is correct, the body would be formed from the orthoquinone by the following series of transformations, which are modelled after those worked out by C. Liebermann† for the corresponding case of beta-naphthoquinone: —



The replacement of the two hydrogen atoms of the orthoquinone by the anilido groups to form II. takes place under the oxidizing influence of another portion of the orthoquinone, which takes up hydrogen to form pyrocatechine (always formed in our process); II. then passes by isomerization into III., which is converted into IV. by the further action of aniline.

Upon treating the solution of orthoquinone with orthophenylenediamine no phenazine was formed, but the reaction seemed to consist only in the oxidation of the diamine.

We have also devoted some attention to the study of the tetrabromorthoquinone, and have obtained from it two derivatives. The first of these was prepared by treating tetrabromorthoquinone with tetrabrompyrocatechine dissolved in acetic acid and water; it was a beautiful red

* Ann. chem. (Liebig), CCCXI. 276.

† Ber. d. chem. Ges., XIV. 1664.

body, which was soluble only in warm nitrobenzol. Its formula was $C_{12}Br_6O_4$, and it was formed by the following reaction:

$$C_6Br_4(OH)_2 + C_6Br_4O_2 = C_{12}Br_6O_4 + 2HBr,$$

as was shown by the detection of hydrobromic acid as one of the products of the reaction, and the fact that a good yield was obtained only when the two reagents were used in equal amounts. This formation of the substance is most naturally explained by supposing that the two benzol rings are united together by two of the atoms of oxygen forming a substituted pyrocatechine ether, $C_6Br_4{=}O_2{=}C_6Br_2O_2$, but it is also possible that the union took place directly between the two benzol rings forming a diyhenyl compound with this formula, $O_2Br_2C_6{-}C_6Br_2O_2$, the two atoms of bromine removed in this reaction combining with the atoms of hydrogen of the pyrocatechine, and thus oxidizing it so that the body contains two orthoquinone groups. To decide between these two formulas the substance was submitted to reduction with sodium amalgam, as under these circumstances the pyrocatechine ether should be split into two molecules of pyrocatechine, while the diphenyl compound should be reduced without splitting the molecule. The principal product of this reduction was a chocolate brown substance, which contained an amount of bromine nearly identical with that of the original body, and was converted into it again by nitric acid. With it there was always formed a certain amount of pyrocatechine, and this seemed to us strongly in favor of the ether formula, but it could not be considered conclusive, as the amount of pyrocatechine was much less than that of the brown product. In the hope of increasing the yield of pyrocatechine we submitted the brown product again to the action of sodium amalgam, but found it was entirely unaffected; we accordingly oxidized it to the original red body, — a reaction which takes place quantitatively, — reduced this again by sodium amalgam, obtaining fresh quantities of pyrocatechine and the brown body, and continued these alternate reductions and oxidations until the original specimen of the red body had been completely converted into pyrocatechine. Although we could wish that this conversion had taken place by reduction alone, the use of the oxidations cannot be held to vitiate the argument, as they gave a quantitative yield of the original substance, and we feel justified, therefore, in inferring that the two benzol rings are united by two atoms of oxygen, and that the substance is a pyrocatechine ether.

The brown product formed by the action of sodium amalgam was also obtained by the action of tribrompyrogallol on the tetrabromorthoqui-

none, and of hydrochloric acid at 160° to 175° on the red pyrocatechine ether. There seems no doubt, therefore, that it is formed from the red body by the conversion of two orthoquinone oxygen atoms into hydroxyl groups; in other words, that it is the pyrocatechine corresponding to the red orthoquinone; and this view is confirmed by the oxidation of the brown substance to the red by nitric acid. The reaction of the hydrochloric acid is especially instructive in regard to the constitution of these two bodies, as it is the familiar conversion of a quinone to a hydroquinone by this reagent. The red color of the original substance also points to the presence of orthoquino oxygen in it, whereas the lighter color of the reduction product (brown when crystallized, but purplish white when amorphous) confirms the view that it is the hydroxy compound. We therefore assign the following formulas and names to these substances, — red compound, $Br_4C_6{=}O_2{=}C_6Br_2O_2$, hexabromorthoquinopyrocatechine ether; the brown reduction product, $Br_4C_6{=}O_2{=}C_6Br_2(OH)_2$, hexabromdiorthoxypyrocatechine ether. The only observed fact not in accordance with this last formula is that the substance does not dissolve in a solution of sodic hydrate, as we should expect it to do considering that it contains two phenol hydroxyls; this may, however, be explained by the very slight solubility of the substance (soluble only in warm nitrobenzol), which might prevent the solution of sodic hydrate from coming into sufficiently close contact with it to react.

The hexabromorthoquinopyrocatechine ether was formed when acetic acid or alcohol was used as the solvent, but none of it was obtained when the tetrabromorthoquinone and tetrabrompyrocatechine were mixed in solution in chloroform or ether. In this latter case the residue left after the evaporation of the solvent was a reddish white mass, apparently a mixture of the unaltered reagents, which contained none of the hexabromorthoquinopyrocatechine ether. This is strange, as Zincke by mixing the two substances in ethereal solution obtained a black crystalline substance. An attempt will be made in this laboratory next year to find the conditions under which this black compound is formed.

We have succeeded also in obtaining a reaction similar to that just described from tribromresorcine and tetrabromorthoquinone. The other phenols tried acted simply as reducing agents. The product proved to be a ditribrommetoxyphenyldibromorthoquinophenylene ether,

$$(C_6HBr_3OHO)_2C_6Br_2O_2.$$

This substance melts at 217°, and like the reduction product just described, does not dissolve in a solution of sodic hydrate, in spite of the two

phenol hydroxyl groups it contains, according to its most probable formula. We should explain this anomaly in the same way as before, although this substance is much more soluble than the reduction compound.

With glacial acetic acid the tetrabromorthoquinone $C_6Br_4O_2$ formed a white compound, to which we have given much attention, but of which we can only give a very imperfect account. Zincke * in his paper on tetrabromorthoquinone noticed that it was attacked by glacial acetic acid, but did not isolate the product; on the other hand he obtained a white body by crystallizing tetrabromorthoquinone from ether and ligroin, which we have not succeeded in encountering. When tetrabromorthoquinone is evaporated to dryness with glacial acetic acid, a small amount of the red hexabromorthoquinopyrocatechine ether is formed, but the greater part of the quinone is converted into a white crystalline body melting at 230°, the analysis of which led to one of the two following formulas, $C_{14}H_2Br_8O_5$ or $C_{14}Br_8O_5$. The first would be formed by the union of two molecules of the tetrabromorthoquinone with one of acetic acid, one molecule of water being eliminated, thus: —

$$2C_6Br_4O_2+C_2H_4O_2=C_{14}H_2Br_8O_5+H_2O.$$

The second would be formed from the first by removing two atoms of hydrogen, which could be done by the oxidizing action of another portion of the tetrabromorthoquinone, and the tetrabrompyrocatechine thus formed would then give rise to the red body, which always accompanied the white product; but the amount of this red compound always fell far below that which should be formed, if it had taken such an important part in the reaction (10 grams of tetrabromorthoquinone should give 5 grams of the red product, whereas the usual yield was only 0.8 gram), and, as the amount of hydrogen found in the white compound was distinctly larger than should have been given by a body free from that element, we have decided to adopt provisionally the formula $C_{14}H_2Br_8O_5$. We had hoped to settle this question by studying the decomposition products of this substance, but so far it has either been unaffected or completely decomposed by all the reagents we have tried. We hope that in the coming year the study of this body will be completed and the work carried on in various other directions in this Laboratory.

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* Ber. d. chem. Ges., XX. 1777.

Experimental Part.

Action of Iodine on the Lead Salt of Hydroquinone.

These experiments were tried to test the efficacy of this method of making quinones. An aqueous solution of ten grams of hydroquinone was treated with the calculated amount of sodic hydrate in a flask, to which the air had access only through a tube containing an alkaline solution of pyrogallol; to the sodium salt thus formed an aqueous solution of plumbic acetate was added, which gave a white precipitate of the lead salt. As this blackened rapidly on exposure to the air, no attempt was made to filter it, but an alcoholic solution of five grams of iodine was added directly to the precipitate suspended in the liquid, when plumbic iodide was formed, as shown by the appearance of a yellow color. After the reaction seemed to have come to an end, the insoluble substances were filtered out, and the filtrate, which had a strong odor of quinone, extracted with ether. This ether extract left on evaporation yellow crystals with a strong odor of quinone, which under the microscope showed the characteristic form of this substance, and after purification by sublimation melted at 112°–113°, which, although distinctly below the melting point of quinone, 115°.7, is near enough to it to prove in conjunction with the other properties that quinone was formed.

To prove that this quinone was formed by the action of the iodine on the lead salt and not by the oxidizing effect of the air, a specimen of the salt mixed with water was exposed to the air for several hours, until it was thoroughly blackened; upon filtration a red solution was obtained which had no odor of quinone. Extraction with ether did not remove the red color, and on the evaporation of the ether, crystals of hydroquinone were obtained, recognized by the melting point, but no quinone. Upon adding an alcoholic solution of iodine to a similar specimen of the lead salt blackened by exposure to the air, the sharp odor of quinine was observed at once, and a considerable amount of this body was obtained from the filtrate. The method, therefore, is applicable to the production of quinones, but naturally would be used only in cases where oxidation is inadmissible.

We also tried some experiments with iodine and the lead salt of resorcine, but as it was evident that the purification of the product would be a matter of great difficulty, we have postponed the continuation of this work until we have finished the study of pyrocatechine.

Orthoquinone.

Action of Iodine on the Lead Salt of Pyrocatechine, Preparation of a Solution of Orthoquinone.

To prepare the lead salt of pyrocatechine two grams of pyrocatechine dissolved in 150 c.c. of water were added gradually, with constant stirring, to a boiling solution of 7.5 grams of plumbic acetate in 250 c.c. of water. The precipitated lead salt was allowed to settle, filtered out, and washed five times with hot water. It was then dried at 100°, and finely pulverized. It is not advisable to use more than two grams of pyrocatechine at a time in making the lead salt, as with larger amounts it was found to be hard to wash out all the impurities.

Ten grams of this lead salt were thoroughly moistened with chloroform in a 500 c.c. glass-stoppered flask. The salt must be absolutely dry, and the chloroform free from water and alcohol, as these substances decompose orthoquinone. A boiling solution of five grams of iodine in 200 c.c. of chloroform was then added to the lead salt and the whole shaken well for five to ten minutes; after which, upon filtering through a dry Gooch crucible, a garnet red solution of orthoquinone was obtained. The amount of iodine used in this experiment is a little more than half that required by the theory (one molecule to each molecule of the lead salt). This large excess of the lead salt was used to avoid as far as possible the presence of iodine in the chloroform solution, and in this we were fairly successful, as a sample of it, when tested with a fresh specimen of the lead salt of pyrocatechine, showed only a trace of plumbic iodide.

This chloroform solution contained orthobenzoquinone, $C_6H_4O_2$ 1.2, as is proved by the experiments described later in this paper, and it must have been a nearly pure solution of this body, since the only other substance which could have been present was iodine, and the amount of this was very small, as shown in the preceding paragraph. It had a dark garnet red color, and no odor could be perceived except that of the chloroform. Within an hour from the time of its preparation it began to show signs of alteration by depositing a black precipitate, and after twenty-four to thirty hours all the orthoquinone had disappeared from the solution. We have made numerous attempts to isolate the solid quinone from its solution in chloroform, of which the following is a brief summary: Evaporation spontaneously at ordinary temperatures; evaporation at −12°; evaporation *in vacuo* of a solution in pure chloroform made from chloral, so as to avoid all traces of alcohol which decomposes

the orthoquinone; evaporation by a stream of dry air, or dry carbonic dioxide passed through the solution cooled by a freezing mixture; precipitation with ligroin at —5°; precipitation with tetrachloride of carbon at —20°; we had great hopes of this last attempt, as we had not succeeded in making any of the orthoquinone, when tetrachloride of carbon was substituted for chloroform in the preparation, and we inferred from this that the quinone probably was insoluble in this substance; but this, as well as all the other experiments mentioned above, did not lead to the desired result. The product in every case was the black alteration product already mentioned, the nature of which will be discussed presently, so that we are forced to the conclusion that the orthobenzoquinone cannot exist for any length of time, if at all, in the solid state.

Study of the Alteration Product of Orthobenzoquinone.

This substance was most conveniently obtained by allowing the chloroform solution of orthobenzoquinone, prepared as already described, to stand at ordinary temperatures in a corked flask from twenty-four to thirty hours.* The black precipitate thus formed was not easy to purify, for although it was soluble in alcohol and some other solvents, all our attempts to crystallize it have failed; we finally decided to depend for its purification on its insolubility in chloroform and benzol. Accordingly, after filtering it out from the chloroform in which it was formed, we washed it thoroughly with chloroform, and afterward extracted it three times with hot benzol. About 40 per cent of the orthoquinone used was converted into this black product. In calculating this yield we assumed that the amount of orthoquinone in the chloroform solution corresponded to the amount of iodine used in making it. The black substance, after it had been purified by extraction with benzol, was dried *in vacuo* and analyzed with the following results: —

0.2041 gram of the substance gave on combustion 0.4684 gram of carbonic dioxide and 0.0696 gram of water.

	Calculated for $C_{12}H_2O_2(OH)_2$.	Calculated for $C_{13}H_6O_2(OH)_2$.	Found.
Carbon	66.67	62.07	62.59
Hydrogen	3.70	3.45	3.79

These numbers would indicate that the substance has been formed by the union of two molecules of orthoquinone with the introduction of a

* The solution should not be allowed to stand more than thirty hours, as in that case the product is contaminated with a brown impurity.

hydroxyl group, but it is obvious that the composition of a body like this, which is amorphous, and has no definite melting point, can be determined only by the analysis of several samples prepared by different methods. Accordingly we undertook the preparation and analysis of the lead salt, which should be insoluble and stable, if the substance contains two hydroxyls in the ortho position to each other, as would be the case if it is formed from two molecules of orthoquinone. Further, as we thought that the additional hydroxyl indicated by the analysis might have been introduced by the action of the oxygen of the air, we repeated the preparation in an atmosphere of carbonic dioxide. The solution of orthoquinone was made from the lead salt of pyrocatechine and iodine in a flask filled with this gas, and was separated from the plumbic iodide by means of a rose filter with an asbestos film without exposing it to the air. Upon standing over night still in an atmosphere of carbonic dioxide, a black precipitate was formed identical in appearance with that obtained by the ordinary process. This was purified in the way already described, and then converted into its lead salt as follows: 0.3 gram of this black body dissolved in 40 c.c. of alcohol was added to a boiling solution of one gram of plumbic acetate in 400 c.c. of water; this large amount of water is necessary to prevent the alcohol from precipitating plumbic acetate, which, becoming imprisoned in the lead salt, could hardly be removed by washing. The jet black lead salt thus obtained was washed five times with hot water, dried at 100°, and analyzed with the following result: —

0.2352 gram of the salt gave 0.1645 gram of plumbic sulphate.

	Calculated for $C_{12}H_6O_2O_2Pb$.	Calculated for $C_{12}H_5O_2OHO_2Pb$.	Found.
Lead	49.17	47.39	47.76

This result shows that the oxidizing agent, which introduces the additional hydroxyl, is not the oxygen of the air, but the orthoquinone itself, and this view is confirmed by the fact that the chloroform solution, from which the black compound has separated, contains brown substances probably formed from the orthoquinone in oxidizing the insoluble product, but which were so unmanageable that we were unable to determine their composition.

We would add here two analyses made by H. A. Torrey some years ago in this laboratory with a body agreeing with our black compound in its properties, which he had prepared by the electrolytic oxidation of pyrocatechine. They gave the following results: —

I. 0.1275 gram of the substance gave on combustion 0.2940 gram of carbonic dioxide and 0.0436 gram of water.

II. 0.0608 gram of the substance gave 0.1401 gram of carbonic dioxide and 0.0230 gram of water.

	Calculated for $C_{12}H_3O_3(OH)_3$.	Found. I.	Found. II.
Carbon	62.07	62.88	62.85
Hydrogen	3.45	3.80	4.20

The substance is obviously the same as that previously analyzed, although not so pure.

We have, therefore, four analyses of three samples of this substance prepared or purified in different ways, and, as these agree, there can be no doubt that the black alteration product of the orthoquinone is a definite compound, and has the composition $C_{12}H_3O_5$.

*Properties of the Black Alteration Product of Orthobenzoquinone (Orthodioxyphenyloxyorthoquinone,** $C_6H_3(OH)_2C_6H_2OHO_2$). — It forms an almost black amorphous powder, which does not melt, but decomposes gradually at temperatures above 170°. It is easily soluble in cold alcohol, ether, or glacial acetic acid; insoluble in benzol or chloroform, whether cold or hot. Strong acids have no apparent action on it, but alkalies dissolve it.

The following experiments were undertaken to determine the constitution of the black alteration product.

Reduction of the Alteration Product.

The formula of the substance $C_{12}H_3O_5$ indicates that it contains two benzol rings, and these may either be united directly, forming a diphenyl compound, or they may be united by two atoms of oxygen, forming a substituted pyrocatechine ether, $[C_6H_3OH]O_2[C_6H_2(OH)_2]$. The diphenyl formula, $(HO)O_2H_2C_6\text{-}C_6H_3(OH)_2$, is rendered probable by the formation of the dinaphthyldiquinhydrone † under somewhat similar circumstances from beta-naphthoquinone, which has been proved to be a dinaphthyl compound; ‡ the pyrocatechine ether formula, on the other hand, is in harmony with a derivative of tetrabromorthoquinone, which is described later in this paper. Reduction seemed the easiest way to de-

* This name and formula for the substance are established by the work described later in this paper.

† Ann. Chem. (Liebig), CXCIV. 205.

‡ Ibid. 206. Korn Ber. d. chem. Ges., XVII. 3020.

cide between these formulas, as the ether should be split into pyrocatechine and a trioxybenzol, while the diphenyl product would be reduced without splitting apart the two benzol rings. Upon treating the black alteration product with sodium amalgam and water in an atmosphere of carbonic dioxide for several days, an uninviting black solid was obtained on acidification, which was soaked in water, and this water as well as the acidified filtrate from the reduction extracted with ether, but not a trace of pyrocatechine was obtained. As the bromether, which we have obtained in another part of our work, gives a large quantity of pyrocatechine by this treatment, we infer that the black alteration product is a diphenyl derivative.

Action of Benzoylchloride on the Black Alteration Product.

Half a gram of this substance was dissolved in 10 c.c. of a solution of potassic hydrate (1 : 5), and to the warm solution benzoyl chloride was added drop by drop, until the product of the reaction rose to the surface as an oily mass, leaving the liquid clear. This was then treated with sodic hydrate, in which it did not dissolve, and thoroughly washed with water. The tarry mass thus obtained was dissolved in chloroform, the solution filtered, and the filtrate mixed with an excess of alcohol, which preciptated out the substance. After drying *in vacuo* it was analyzed, with the following result: —

0.2210 gram of the substance gave on combustion 0.5933 gram of carbonic dioxide and 0.0744 * gram of water.

	Calculated for $C_{12}H_6O_3(OCOC_6H_5)_3$.	Calculated for $C_{12}H_5O_3(OCOC_6H_5)_3$.	Found.
Carbon	70.91	72.79	73.21
Hydrogen	3.64	3.68	3.74

The substance is therefore a tribenzoyl compound, and the original black body must have contained three hydroxyl groups. This *benzoxyorthoquinoorthodibenzoxydiphenyl*, $C_6H_2(OCOC_6H_5)O_2C_6H_3(OCOC_6H_5)_2$, † forms a light yellow amorphous powder without a definite melting point. It is easily soluble in chloroform; insoluble in alcohol or water. Alkalies do not dissolve it.

The fact that only three benzoyl groups are taken up by the black alteration product indicates that two of its five atoms of oxygen do not

* A little water was lost in this analysis.

† The distribution of the benzoxy groups in this substance has not been determined.

form part of hydroxyl groups; from the formation of the substance these two atoms of oxygen must either belong to a quinone, or be the connecting atoms of a pyrocatechine ether, and, as our work on the reduction of the alteration product has shown that it is probable they are not pyrocatechine ether oxygen atoms, there can be little doubt that they occur in the quinone configuration, which indeed was the more probable supposition of the two. We tried to confirm this inference by the formation of hydrazones both from the original black alteration product and its benzoyl derivative, but without satisfactory results. When phenylhydrazine in excess was added to a solution of 0.5 gram of the black alteration body dissolved in 10 c.c. of alcohol, the dark blackish color of the solution was discharged, and on pouring the product into acidified water a golden yellow precipitate was formed; but an analysis of the substance gave 6.39 per cent of nitrogen, whereas the most probable formula, $C_{12}H_8O_4NNHC_6H_5$, requires 8.70 per cent of nitrogen. The tribenzoyl derivative of the black substance was dissolved in chloroform, and boiled with an excess of phenylhydrazine for several minutes; a new compound was formed, which was obtained by allowing the chloroform to evaporate spontaneously, treating with an acid to remove the excess of phenylhydrazine, dissolving the residue in cold alcohol, and precipitating the substance from this solution with water. After drying *in vacuo* it was analyzed, and 3.19 per cent of nitrogen found instead of 4.42 per cent of nitrogen required by the formula of the hydrazone, $C_{12}H_5O(NNHC_6H_5)(OCOC_6H_5)_3$. It is evident from these results that phenylhydrazine acts on both of these substances, and that the product in each case contains nitrogen. The results, therefore, as far as they go, confirm our inference that there are two quinone atoms of oxygen in the black substance, but they are of little value, because the exceedingly unmanageable nature of both of these substances prevented us from purifying them sufficiently to determine their composition with certainty.

The work just described establishes the following points with tolerable certainty. The black alteration product is a diphenyl compound, and contains three hydroxyl groups and an orthoquinone group; it may therefore be called orthodioxyphenyloxyorthoquinone, and receive the formula $C_6H_3(OH)_2C_6H_2(OH)O_2$, although the three hydroxyl groups may be attached to the same benzol ring, as we have not determined the position of the third hydroxyl experimentally.

Experiments with the Solution of Orthobenzoquinone.

Action of Hydrochloric Acid on the Solution of Orthobenzoquinone.

Dry hydrochloric acid gas was passed through a fresh chloroform solution of orthoquinone (prepared from iodine and the lead salt of pyrocatechine), until it fumed strongly. After filtering out a slight tarry precipitate, a large part of the chloroform was recovered by distillation, and the concentrated solution thus obtained allowed to stand over night in an open vessel. The residue, which was usually oily, was heated on the steam-bath to drive off the last traces of the solvent and a slight impurity of iodine, and then extracted with a hot mixture of three parts chloroform with one of ligroin, which left behind a large quantity of a black oil. The solution became milky on standing, and deposited an oily substance, followed, when it had cooled, by the formation of crystals. As soon as these crystals began to appear the clear solution was decanted from the oil and allowed to crystallize in a separate vessel. The residual oils by a similar treatment with chloroform and ligroin yielded an additional amount of the crystals. The crystals were dissolved in benzol, and treated with bone-black, after which they were purified by repeated crystallizations from the mixture of chloroform and ligroin. They showed the melting point 84° to 85°, which was not quite constant, indicating that the substance was not perfectly pure; but in spite of this it was dried *in vacuo*, and analyzed with the following result: —

0.2005 gram of the substance gave by the method of Carius 0.1865 gram of argentic chloride.

	Calculated for $C_6H_3Cl(OH)_2$.	Found.
Chlorine	24.57	23.00

This result indicates that the body is monochlorpyrocatechine, but that it contains some pyrocatechine, as would be expected if the reaction ran in the same way as that of hydrochloric acid on parabenzoquinone, since Wichelhaus * has shown that in this case hydroquinone and chlorine are formed in the first instance, and that the substitution compounds, which form the final product, are made by the action of the chlorine on the hydroquinone. We have not attempted to purify the chlorpyrocatechine more thoroughly, as much time and labor would be necessary to obtain sufficient material for this purpose, and the forma-

* Ber. d. chem. Ges., XII. 1504.

tion of chlorpyrocatechine under these conditions is confirmed by the following analysis of the lead salt, made by adding plumbic acetate to an aqueous solution of the product of the reaction of hydrochloric acid on the solution of orthoquinone.

0.3867 gram of the salt gave .03306 gram of plumbic sulphate.

	Calculated for $C_6H_3ClO_2Pb$.	Found.
Lead	58.98	58.55

The monochlorpyrocatechine in the slightly impure state in which we obtained it crystallized in white pearly plates, which are easily soluble in water, alcohol, ether, benzol, chloroform, or acetone; insoluble in ligroin. With an aqueous solution of plumbic acetate it gives a lead salt. It blackens quickly if exposed to the air after treatment with an alkali. The melting point observed by us is of course of no value, on account of the presence of the impurity of pyrocatechine.

Behavior of the Solution of Orthobenzoquinone with Reducing Agents.

Ammonic Sulphide. — Some of the solution of orthoquinone in chloroform was shaken with about one third of its volume of the ordinary laboratory solution of ammonic sulphide. The red color of the orthoquinone disappeared, and the aqueous solution took on a dark color. The two liquids were separated by means of a drop funnel, and the chloroform was extracted twice with water, the extracts being added to the ammonic sulphide solution at first obtained. The mixed aqueous portion was then heated on the steam bath, acidified with hydrochloric acid, allowed to stand until the precipitated sulphur had settled, filtered, and the clear dark colored filtrate extracted with ether. The residue left on the evaporation of the ether was recrystallized twice from benzol, when it was found to melt constant at 103°–104°, and to show all the other properties of pyrocatechine. In order to be certain that the pyrocatechine, detected in the product from the action of ammonic sulphide on the orthoquinone solution, was formed from the orthoquinone, it was necessary to prove that this solution contained no free pyrocatechine; for this purpose a small amount of it taken before the reduction was shaken with water, the water evaporated, and the residue extracted with benzol; the benzol extract was evaporated to dryness, the very slight residue dissolved in water, and tested with plumbic acetate, when it gave no precipitate, showing that no free pyrocatechine was contained in the chloroform solution.

Action of Sulphurous Dioxide. — Dry sulphurous dioxide was passed through the chloroform solution of orthoquinone until it was saturated; the principal product was a black unmanageable precipitate, probably a compound of orthoquinone and pyrocatechine corresponding to chinhydrone; but the filtrate from this left on evaporation crystals, which were recognized as pyrocatechine by their properties and the formation of the lead salt.

Action of Bromine on the Solution of Orthobenzoquinone.

An excess of bromine was added to the solution of orthoquinone in chloroform, the chloroform allowed to evaporate spontaneously, and the crystalline residue, after being heated gently to drive off the excess of bromine, was spread on unglazed porcelain to remove oily impurities. After recrystallization from benzol it showed the constant melting point 191°, which is near enough to 192°–193°, that given by Zincke* for tetrabrompyrocatechine to leave no doubt as to the nature of the substance. For greater certainty the substance was analyzed with the following results: —

I. 0.1835 gram of the substance gave by the method of Carius 0.3210 gram of argentic bromide.

II. 0.1509 gram of the substance gave 0.2637 gram of argentic bromide.

	Calculated for $C_6Br_4(OH)_2$.	Found. I.	Found. II.
Bromine	75.11	74.44	74.39

These numbers are sufficiently near to show that the product of the action of bromine on the orthobenzoquinone is tetrabrompyrocatechine.

Behavior of the Solution of Orthobenzoquinone with Benzolsulphinic Acid.

The chloroform solution of orthoquinone was added drop by drop to a solution of benzolsulphinic acid,† also in chloroform, until the color began to disappear less rapidly, and the solution of the sulphinic acid had assumed a decided reddish tint. After standing over night, the liquid was filtered, the filtrate evaporated to dryness, and the residue allowed to solidify. The solid residue was next treated with hot benzol, which

* Ber. d. chem. Ges., XX. 1777.

† If the conditions were reversed, and the solution of benzolsulphinic acid was added to the solution of orthoquinone, none of the desired sulphone was obtained; we ascribe this difference in behavior to the oxidation of the sulphinic acid by the excess of orthoquinone.

dissolved all but a slight black residue. On allowing the benzol solution to evaporate a crystalline substance was obtained, which was purified by crystallizations with the aid of bone-black at first from water mixed with a little alcohol, finally from water alone, until it showed the constant melting point 153°, when it was dried at 100°, and analyzed with the following results: —

I. 0.2353 gram of the substance gave on combustion 0.4931 gram of carbonic dioxide and 0.0862 gram of water.

II. 0.1454 gram of substance gave by the method of Carius 0.1418 gram of baric sulphate.

	Calculated for $C_6H_3(OH)_2SO_2C_6H_5$.	Found. I.	Found. II
Carbon	57.60	57.14	
Hydrogen	4.00	4.07	
Sulphur	12.80		13.39

As this body must be a substituted pyrocatechine, it should give a lead salt, and upon trying it with a solution of plumbic acetate we obtained one, which was analyzed with the following result: —

0.2601 gram of the substance gave 0.1729 gram of plumbic sulphate.

	Calculated for $C_6H_3O_2PbSO_2C_6H_5$.	Found.
Lead	45.50	45.39

There can be no doubt, therefore, that the substance is a pyrocatechinesulphone or orthodioxydiphenylsulphone.

Properties of Orthodioxydiphenylsulphone, $C_6H_3(OH)_2SO_2C_6H_5$. — It crystallizes from alcohol and water in short, thick, well-formed, white prisms terminated by two planes at an obtuse angle to each other. It contains no water of crystallization, and melts at 153°. It is easily soluble in alcohol, ether, chloroform, or glacial acetic acid; very slightly soluble in cold water, or benzol, freely soluble in either of these liquids when hot; essentially insoluble in ligroin, either hot or cold. Alkalies dissolve it with a yellow color. Ferric chloride gives a bluish green color with it, which changes to red on the addition of sodic carbonate. As has been already mentioned, its aqueous solution gives a precipitate with plumbic acetate.

This substance has the same composition as the orthodioxydiphenylsulphone made by Hinsberg and Himmelschein * by oxidizing pyrocate-

* Ber. d. chem. Ges. XXIX. 2025.

chine in presence of benzolsulphinic acid, and we should expect that the two bodies would be identical, but, strangely enough, they seem to be isomeres, since Hinsberg and Himmelschein's compound contains water of crystallization, and melts in presence of this at 117° ; when dried in the steam oven, at 143°–145° ; when previously fused in the air, at 164° ; whereas our substance contains no water, and melts at 153°, whether dried at ordinary temperatures or by previous fusion. We made five attempts to prepare their body according to Hinsberg and Himmelschein, but did not succeed in finding the conditions under which it is formed, which must lie within very narrow limits ; and, as in doing this we had devoted more time to the subject than we could afford, we were obliged to abandon our intention of making a comparative study of the two compounds.

Action of Aniline on the Solution of Orthobenzoquinone.

The solution of orthoquinone in chloroform was heated with an excess of aniline for five minutes on the steam-bath ; the chloroform was then allowed to evaporate, and the residue, after having been freed from aniline by treatment with hydrochloric acid and washing with water, was purified by recrystallization from a mixture of two parts of alcohol to one of benzol, until it showed the constant melting point 203°, when it was dried at 100°, and analyzed with the following result : —

0.2909 gram of the substance gave 28.2 c.c. of nitrogen at a temperature of 22° and a pressure of 774 mm.

	Calculated for $C_6H_2(C_6H_5NH)_2C_6H_5NO$.	Found.
Nitrogen	11.51	11.27

The substance is therefore a dianilinoquinoneanil. When the aqueous wash waters obtained in the preparation of this substance were extracted with ether, pyrocatechine was obtained, recognized by its odor and lead salt.

Properties of the dianilinoquinoneanil, $C_6H_2(C_6H_5NH)_2C_6H_5NO$. — Crystallized from alcohol and benzol it forms bronze-colored small needles melting at 203°, although they begin to draw together somewhat at 198°. The melting point of this substance is identical with that (202°–203°) given by Zincke and Hagen * for the dianilinoquinoneanil made from paraquinone by the action of aniline and glacial acetic acid,

* Ber. d. chem. Ges., XVIII. 787.

and, as a comparison of the two substances showed they crystallized in the same form, there can be no doubt of their identity. The formation of a paraquinone derivative from our orthoquinone has been already explained in the introduction to this paper.

In the hope of obtaining a phenazine the solution of orthoquinone was treated with orthophenylene diamine; a reaction took place, the principal products of which consisted of uninviting black substances and pyrocatechine recognized by the formation of its lead salt. From the appearance of the pyrocatechine we inferred that the reaction consisted principally in the oxidation of the diamine by the orthoquinone, and as even after trying the experiment under several varying conditions no more promising results were obtained, this line of work was abandoned. Phenol also gave with the solution of orthoquinone such an uninviting product that we did not attempt to study it. Sodic hydrate gives with the orthoquinone solution a green coloration similar to that obtained by the action of sodic hydrate on tetrabromorthoquinone.

Derivatives of Tetrabromorthobenzoquinone.

The tetrabromorthoquinone used in this work was prepared as follows: 20 grams of pyrocatechine were dissolved in 50 c.c. of glacial acetic acid, and 37 c.c. of bromine added gradually from a burette. The mixture was allowed to stand over night, after which the product was purified by recrystallization from 200 c.c. of glacial acetic acid. In this way forty grams of pyrocatechine yielded 118–126 grams of recrystallized tetrabrompyrocatechine; that is, between 75 and 80 per cent of the theoretical yield. To convert this tetrabrompyrocatechine into tetrabromorthoquinone thirty grams of it were dissolved in 300 c.c. of glacial acetic acid by heating on the water-bath; the solution was then cooled to 16°, or until the glacial acetic acid began to solidify, and eleven grams of fuming nitric acid of specific gravity 1.5 diluted with 60 c.c. of glacial acetic acid added rapidly, the mixture being kept cool and stirred vigorously during the addition; after standing for five minutes 300 c.c. of water were added, and stirred in thoroughly. If the process had run successfully, the tetrabromorthoquinone settled to the bottom in a glistening mass of dark red crystals, which were filtered off, and dried. The product thus obtained melted at 145°–147° instead of 150°–151°, but was pure enough for our work, which was fortunate, as recrystallization from glacial acetic acid is attended by a great loss of material. Thirty grams of tetrabrompyrocatechine gave eighteen grams of tetrabromorthoquinone, which amounts to about 60 per cent of the theoretical yield.

As has just been stated, the crystallization of tetrabromorthobenzoquinone from glacial acetic acid cannot be effected without considerable loss, which we found was due to the conversion of the tetrabromorthoquinone into two new bodies, one of which was red, the other white.* A more careful study of the conditions under which the red body was formed showed us that it was produced by the action of the orthoquinone with tetrabrompyrocatechine, either existing as an impurity in our tetrabromorthoquinone, or formed from it by reduction. After this the study of this red product was carried on with comparatively little difficulty.

Preparation of Hexabromorthoquinopyrocatechine Ether, $C_{12}Br_6O_4$.

Eleven grams of tetrabromorthoquinone and ten grams of tetrabrompyrocatechine were dissolved in 470 c.c. of glacial acetic acid by heating the mixture on the steam-bath, 180 c.c. of water were then added, which produced no immediate precipitate, and the mixture allowed to stand in a warm place for twenty-four hours. During this time a red precipitate was formed, which was filtered out, and washed with hot alcohol to remove unaltered tetrabromorthoquinone and pyrocatechine. In this way 10.7 grams were obtained; that is, somewhat over 60 per cent of the theoretical yield. The purification of the substance offered at first some difficulty because it was insoluble in all the common solvents, but later we found that it dissolved to a limited extent in hot nitrobenzol, and proceeded as follows: Two grams of the crude red body were dissolved in 150 c.c. of nitrobenzol by heating the mixture on the steam-bath (at higher temperatures more of the substance will dissolve, but the solution is attended with decomposition). Upon cooling, the solution deposited about 0.7 gram of crystals, which were submitted to a second similar crystallization from nitrobenzol at 100°, after which the product was extracted several times with hot alcohol to remove adhering nitrobenzol, dried at 100°, and analyzed. As the substance does not melt, we had no means of determining whether this treatment had been an efficient purification.

I. 0.1809 gram of the substance gave on combustion 0.1374 gram of carbonic dioxide and 0.038 gram of water.

II. 0.1008 gram of the substance gave by the method of Carius 0.1637 gram of argentic bromide.

III. 0.1129 gram of the substance gave 0.1843 gram of argentic bromide.

* Zincke (Ber. d. chem. Ges., XX. 1777) observed that acetic acid acted on tetrabromorthoquinone but did not isolate the products of the action.

	Calculated for $C_{12}Br_6O_4$.	Found. I.	II.	III
Carbon	20.93	20.71		
Hydrogen	0.	0.23		
Bromine	69.76		69.13	69.49

Properties of Hexabromorthoquinopyrocatechine Ether. — The substance crystallizes from warm nitrobenzol in short slender prisms of a pure vermilion red color; it does not melt, and is insoluble in all the common solvents; nitrobenzol dissolves it especially when warm, but, if the solution is heated above 100°, decomposition sets in, as shown by a change of color. The ordinary strong acids have no effect on it in the cold, but fuming nitric acid dissolves it with decomposition; alkalies do not dissolve it, but the substance turns black after standing with an alkali for a short time. The red color of the substance indicates that it contains two orthoquinone oxygen atoms, and this view is confirmed by its behavior with hydrochloric acid and reducing agents described later.

The red substance is probably formed from tetrabrompyrocatechine and tetrabromorthoquinone by the following reaction: —

$$C_6Br_4(OH)_2+C_6Br_4O_2=C_6Br_4O_2C_6Br_2O_2+2HBr.$$

To test this a new preparation was made as described above, and, after the mixture had stood twenty-four hours, it was diluted with five times its volume of water, the reddish white precipitate formed filtered out, the aqueous filtrate acidified with nitric acid, and treated with argentic nitrate, when a heavy precipitate of argentic bromide was thrown down, showing the presence of hydrobromic acid among the products of the reaction. It was also found that the best yield was obtained when the two reagents were used in the proportion of equal molecules, as required by the reaction. The best solvent to be used in the preparation was glacial acetic acid and water, as already described, but the red body was also formed in dilute alcohol (the proportions used were 0.5 gram of each reagent, 40 c.c. of alcohol, and 10 c.c. of water). On the other hand, no reaction was observed when the solvent was ether or chloroform. One gram of each of the reagents was dissolved in 50 c.c. of ether (care was taken that the substances were free from even a trace of acetic acid), and allowed to stand twenty-four hours. As no precipitate had formed, the ether was allowed to evaporate spontaneously, when a reddish white residue was left, which looked like a mixture of the unaltered reagents, and dissolved completely in hot chloroform. This showed that none of the hexabromorthoquinopyrocatechine ether had been formed, as it is insolu-

ble in chloroform. Another portion of the residue from the ethereal solution was dissolved in glacial acetic acid, and slightly diluted, when a copious deposit of the red body appeared on standing. The fact that we observed no action when the tetrabromorthoquinone and tetrabrompyrocatechine were mixed in ether is strange, since Zincke * states that by the action of these two bodies in ether or benzol he obtained black shining needles, which changed color at 110° and sintered together to a brownish liquid. We are unable to explain this difference in the results of the experiments, but hope that future work may lead us to the conditions necessary for preparing the black substance.

If the substance is formed by the reaction given above, it is probable that the two benzol rings are connected by two of the atoms of oxygen; but this is not necessarily the case, as the product might also be a derivative of diphenyl, in which both rings contain orthoquinone groups. To settle the mode of union of the two benzol rings, we submitted the substance to reduction with sodium amalgam as follows: Ten grams of the red substance were covered with water in a flask, from which all the air was excluded by a stream of carbonic dioxide, 3 per cent sodium amalgam was then added in large excess, and the reaction was allowed to run at ordinary temperatures in the atmosphere of carbonic dioxide for several days. At the end of this time the red substance had been converted principally into a purplish white body, which seemed to resist the further action of the sodium amalgam; it was, therefore, filtered out, and washed with dilute acid and alcohol; the aqueous filtrate from this substance gave no precipitate on acidification, but on subsequent extraction with ether we obtained from the extract a considerable quantity of a white residue, which after several crystallizations from benzol gave the melting point 100° instead of 104°, the true melting point of pyrocatechine; from the form of its crystals, however, and as it gave the lead salt and the characteristic color with ferric chloride, there can be no doubt that it was pyrocatechine. As has been stated, the principal product of this reduction was the purplish white insoluble substance, the weight of which amounted to 6 grams from 10 grams of the red body; it was obvious, therefore, that no safe inference in regard to the constitution of the red substance could be drawn from the appearance of this small proportion of pyrocatechine. Accordingly, in the hope of increasing our yield of pyrocatechine, this purplish white product was submitted to reduction with sodium amalgam under the conditions used in its formation, the

* Ber. d. chem. Ges., XX. 1778.

action in this case being allowed to continue for a week, but, as we had reason to expect from our observations in our first reduction, the substance remained essentially unaltered, not more than a trace of pyrocatechine being formed. Meanwhile we had discovered that the purplish white product was converted by nitric acid into the original red substance, and, therefore, we oxidized the unaltered body from the last reduction, and on reducing this again with sodium amalgam, obtained a fresh amount of pyrocatechine with the purplish white product again. By repeating these alternate oxidations and reductions we have succeeded in converting a sample of the red substance completely into pyrocatechine; a result which, it seems to us, proves that this red body is a pyrocatechine ether and not a diphenyl derivative.

The purplish white product of the reduction of hexabromorthoquinopyrocatechine ether by sodium amalgam mentioned frequently in the preceding paragraph proved to have the same solubilities as the mother substance; that is, it was insoluble in all the common solvents except nitrobenzol. It was accordingly recrystallized three times from boiling nitrobenzol, when, as it does not have a definite melting point, it was assumed to be pure. After extraction with alcohol to remove adhering nitrobenzol it was dried at 100°, and analyzed with the following result: —

0.1215 gram of the substance gave by the method of Carius 0.1974 gram of argentic bromide.

	Calculated for $C_{12}Br_6(OH)_2O_2$.	Found.
Bromine	69.56	69.16

Properties. — The substance crystallizes from hot nitrobenzol in very small chocolate brown crystals, which appear to be short, rather blunt needles. As obtained from reduction it has a purplish white color and a characteristic silky lustre. It does not melt at 300°. It is insoluble in all the common solvents except nitrobenzol. An aqueous solution of sodic hydrate does not dissolve it; fuming nitric acid converts it back into the red substance, from which it was made, as is proved by the following experiment: —

Three grams of the chocolate-colored crystals of the reduction product were mixed with 20 c.c. of glacial acetic acid, and 5 c.c. of fuming nitric acid were added. The solid immediately turned red, and, after the mixture had been thoroughly stirred, it was poured into water, and washed.

The oxidation was then repeated in the same way, and the dried product was found to weigh three grams; the conversion from the chocolate-colored substance to the red body, therefore, takes place quantitatively. The red product was recrystallized from warm nitrobenzol, freed from the excess of nitrobenzol with alcohol, dried at 100°, and analyzed with the following result: —

0.1317 gram of the substance gave by the method of Carius 0.2140 gram of argentic bromide.

	Calculated for $C_{12}Br_6O_4$.	Found.
Bromine	69.76	69.15

There can be no doubt that this substance is the hexabromorthoquinopyrocatechine ether described above.

As to the formula of the chocolate-colored product of the reduction there is a certain amount of doubt. Our analysis shows only that its composition does not differ to a marked extent from that of the red mother substance. Its formation by reduction and its conversion to the original body by nitric acid would indicate that it was the hydroxyl compound corresponding to the red quinone, but, on the other hand, its insolubility in sodic hydrate is hard to reconcile with this view. As this may be due, however, to the very slight solubility of the substance in all solvents, which might prevent the sodic hydrate from coming sufficiently in contact with it to react, we are inclined to consider that it is the hexabromorthodioxypyrocatechine ether, and to assign it provisionally the formula $C_{12}Br_6O_2(OH)_2$. We hope that the study of this substance may be finished in this Laboratory in the near future.

Our attempts to decompose the hexabromorthoquinopyrocatechine ether with sulphuric acid led to no result, as no action was observed even after boiling it for several hours with sulphuric acid of 1.44 or even 1.6 specific gravity; but hydrochloric acid reacted upon it, as is shown by the following experiment: 5 grams of the red body were sealed in a tube with 25 c.c. of strong hydrochloric acid, and heated from 160°–175° for five hours; the product, after washing with water and alcohol, showed a strong resemblance to the purplish white body obtained by the reduction with sodium amalgam. On treating it with fuming nitric acid diluted with glacial acetic acid it turned red at once, so that there can be little doubt of the identity of the two substances. This observation can be satisfactorily explained on the theory already adopted, that the purplish white substance is the dihy-

droxy derivative from the red orthoquinone body, as then this action is the familiar reduction of quinone oxygen by hydrochloric acid. This theory is still further supported by the reduction of tetrabromorthoquinone to the purplish white body by tribrompyrogallol described in the next section.

Behavior of Tetrabromorthoquinone with Tribromresorcine.

After we had found, as just described, that tetrabromorthoquinone reacted with tetrabrompyrocatechine, it became of interest to try the action of the tetrabromorthoquinone with other diatomic phenols, and, as we found that unsubstituted phenols of this class reduced the quinone, — pyrocatechine, for instance, reducing it completely to tetrabrompyrocatechine, — we turned our attention to the bromphenols. Of these, tetrabromhydroquinone in alcoholic solution acted only as a reducing agent, giving bromanil and tetrabrompyrocatechine. Tribrompyrogallol also acted only as a reducing agent, giving tetrabrompyrocatechine, which combined with unreduced tetrabromorthoquinone to give the hexabromorthoquinopyrocatechine ether, and this was converted by further action of the tribrompyrogallol into its purplish white reduction product. With tribromresorcine, on the other hand, a new compound was obtained.

8.4 grams of tetrabromorthoquinone and 7 grams * of tribromresorcine † were dissolved with the aid of heat in 600 c.c. of glacial acetic acid mixed with 400 c.c. of water, and allowed to stand for twenty-four hours. At the end of this time a dingy pink precipitate had formed, which was filtered out, washed, and recrystallized from benzol, until it showed the constant melting point 217°, when it was dried at 100°, and analyzed with the following results: —

I. 0.1389 gram of the substance gave by the method of Carius 0.2173 gram of argentic bromide.

II. 0.1370 gram of the substance gave by the method of Carius 0.2144 gram of argentic bromide.

	Calculated for $(C_6Br_2HOHO)_2C_6Br_2O_2$.	Found. I.	II.
Bromine	66.94	66.58	66.61

* The two reagents were used in the proportion of equal molecules, whereas the analysis of the product showed that two molecules of the resorcine should have been taken for each molecule of the quinone.

† The tribromresorcine was prepared by the method of Benedikt (Monatsh. f. Chem. IV. 227.) by mixing the calculated amount of bromine with resorcine dissolved in glacial acetic acid. The product was purified by crystallization from benzol and ligroin.

The substance, therefore, is evidently formed by the union of two molecules of the resorcine with one of the quinone with elimination of two molecules of hydrobromic acid, and may be called the ditribrom-metoxyphenyldibromorthoquinophenylene ether.

Properties. — It crystallizes from benzol in slender lemon-yellow prisms with square ends, and melts at 217°. It is soluble in ether; slightly soluble in cold alcohol or chloroform, easily soluble in either of these solvents when hot; nearly insoluble in cold benzol, much more soluble in hot benzol, which is the best solvent for it. It does not dissolve in sodic hydrate, which throws some doubt on the formula we have ascribed to it, as this contains two hydroxyl groups.

Action of Glacial Acetic Acid on the Tetrabromorthoquinone.

As has been already stated, tetrabromorthoquinone, when crystallized from glacial acetic acid, is partially converted into a white substance * which we found it convenient to prepare as follows: 10 grams of tetrabromorthoquinone were dissolved in 80 c.c. of glacial acetic acid and the solution slowly evaporated to dryness on the steam-bath, the reddish white residue was moistened with 10 c.c. of glacial acetic, and the slow evaporation on the steam-bath repeated, in order to act on any tetrabromorthoquinone which might have escaped the previous reaction; the residue was then extracted with 200 c.c. of hot alcohol, and filtered boiling, when the red hexabromorthoquinopyrocatechine ether previously described was left behind, as it is insoluble in alcohol. This substance seemed to be a constant product of the reaction, but not a principal one, as the amount was only about 0.8 gram. The alcoholic solution was allowed to cool, and filtered again; then it was diluted with 200 c.c. of water, which precipitated out the white product, amounting to from 5–6 grams. This was purified by crystallization from glacial acetic acid, until it showed the constant melting point 230°, when it was dried at 100°, and analyzed with the following results: —

I. 0.2658 gram of the substance gave on combustion 0.1903 gram of carbonic dioxide and 0.0179 gram of water.

II. 0.1373 gram of the substance gave by the method of Carius 0.2306 gram of argentic bromide.

* Zincke (Ber. d. chem. Ges. XX. 1777) converted tetrabromorthoquinone into a white substance by crystallizing it from a mixture of ether and ligroin. On repeating the experiment we did not succeed in finding the conditions under which the white product is formed.

III. 0.3015 gram of the substance gave on combustion 0.2090 gram of carbonic dioxide and 0.0223 gram of water.

IV. 0.1265 gram gave 0.2122 gram of argentic bromide.

V. 0.1279 gram gave 0.2147 gram of argentic bromide.

VI. 0.1138 gram gave 0.1911 gram of argentic bromide.

VII. 0.1229 gram gave 0.2074 gram of argentic bromide.

	Found.						
	I.	II.	III.	IV.	V.	VI.	VII.
Carbon	19.53		18.90				
Hydrogen	0.75		0.82				
Bromine		71.45		71.39	71.44	71.48	71.83

Of these analyses I. and II. were of samples prepared and purified as described; III. to VII. were of specimens prepared earlier in our work, and in some cases purified by slightly different, and perhaps less effective, methods.

Two determinations of the molecular weight were made by the method of freezing, the solvent being benzol.

I. 0.262 gram of the substance dissolved in 16.58 grams of benzol produced a depression of 0.099°.

II. 0.594 gram of the substance in 16.58 grams of benzol produced a depression of 0.219°.

	I.	II.
Molecular Weight	782	802

The most probable formula to be derived from these data is $C_{14}H_2Br_8O_5$, formed by the union of two molecules of tetrabromorthoquinone with one of acetic acid, one molecule of water being eliminated. The results, however, agree almost as well with $C_{14}Br_8O_5$, although the percentage of hydrogen found is high for a substance which is free from this element. A compound with the formula $C_{14}Br_8O_5$ would be formed by the removal of two atoms of hydrogen from the preceding compound, a reaction which might easily be brought about by the oxidizing action of a portion of the tetrabromorthoquinone; the tetrabrompyrocatechine thus formed in turn acting on the unaltered quinone would give the red body which, as already stated, is always produced with the white substance; but it should be remembered that the quantity of the red body formed is far below that which would be expected from such a reaction.

	Calculated for $C_{14}H_2Br_8O_5$.	Found. I.	Found. II.	Calculated for $C_{14}Br_8O_5$.
Carbon	18.88	19.53		18.92
Hydrogen	0.22	0.75		
Bromine	71.95		71.45	72.07
Molecular Weight	890	782	802	888

It is obvious that the decision can be made between these formulas only by the chemical study of the substance, but unfortunately we have not succeeded as yet in decomposing it by any of the reagents we have tried, so that we must leave this question undecided for the present, with the statement that we consider the formula $C_{14}H_2Br_8O_5$ the most probable. The study of the substance will be continued in this Laboratory next year.

Properties of the Substance $C_{14}H_2Br_8O_5$. — When crystallized from glacial acetic acid it forms small, almost square rhombic plates with a pearly lustre, which melt at 230°. It is easily soluble in ether, benzol, chloroform, acetone, or ethyl acetate; almost insoluble in glacial acetic acid, but its solubility is increased by heat, as the boiling acid takes up from two to three per cent of the substance. Its solubility in ethyl alcohol is similar to that in glacial acetic acid; curiously enough, when first formed, the crude mass is rather freely soluble in alcohol, but, as the purification continues, it becomes less and less so, until, when pure, it is nearly insoluble in cold alcohol, as already stated. It is essentially insoluble in ligroin or in water, hot or cold. The best solvent for it is glacial acetic acid. None of the strong acids dissolve it when cold; nor does even a hot solution of sodic hydrate show any perceptible action with it.

This substance is decidedly stable, as is shown by the following experiments, which were tried in the hope of decomposing it into simpler bodies, in order to throw some light on its nature: 0.5 gram of the white substance were treated with sodium amalgam and water in an atmosphere of carbonic dioxide for eight days. At the end of this time the substance was recovered unaltered, as shown by its melting point. The filtrate was acidified, and extracted with ether, but yielded no pyrocatechine. 0.2 gram of the substance were dissolved in boiling glacial acetic acid, and mixed with 5 c.c. of fuming nitric acid also diluted with glacial acetic acid; no visible reaction took place, and upon dilution with water the original substance was obtained, as shown by the melting point. 0.2 gram were dissolved in cold chloroform, and 3 c.c. of bromine added; after standing for twenty-four hours the chloroform was evaporated,

leaving the original substance, as shown by the melting point. 0.2 gram of the substance were dissolved in benzol, and an excess of aniline added; after standing for twenty-four hours the benzol and aniline were removed, when the unaltered substance was obtained, as shown by the melting point. Phenylhydrazine gave a similar negative result. No action could be observed when the substance was treated with an alkaline solution of potassic permanganate, or was boiled with sulphuric acid of specific gravity 1.44 or 1.6, or heated to 150° in a sealed tube with hydrochloric acid. If it was heated to 250° with hydrochloric acid, the compound was completely destroyed, and complete destruction also ensued when it was treated with fuming nitric acid, or a solution of chromic anhydride, or when it was fused with potassic hydrate. In continuing this work next year renewed attempts will be made to obtain decomposition products of the substance, and efforts will also be made to throw light on its constitution by preparing allied compounds.

It should also be mentioned that acetacetic ester converts tetrabromorthoquinone into tetrabrompyrocatechine, which then forms hexabromorthoquinopyrocatechine ether with unaltered tetrabromorthoquinone. Chloral showed no action with tetrabromorthoquinone even at 100°. The study of the little-known and very reactive tetrabromorthoquinone will be continued in various directions in this Laboratory.